Lay, 1986). Likewise the average of the other N···Cl$^-$ distances (3·414 Å) is similar to that in the chloride salt (3·457 Å).

The motivation for determining the present structure was to obtain a comparison with $[Ru(NH_3)_5Cl]Cl_2$. The precisely determined Ru—Cl bond lengths are not significantly different, 2·343 (1) and 2·346 (1) Å. Likewise the average Ru—N bond lengths are very similar, 2·108 and 2·103 Å. Thus, the present results are contrary to arguments that analyses of trends in M—X bond distances must be qualified because these distances may be significantly affected by crystal-packing and hydrogen-bonding effects (Monsted & Monsted, 1989). In the present structure, the coordinated Cl atom is involved in one hydrogen bond only and in $[RuCl(NH_3)_5]Cl_2$ it is involved in two, yet the bond lengths are indistinguishable. The ammine groups are hydrogen bonded to Cl$^-$ and BF_4^- anions in the present structure and only to Cl$^-$ in $[RuCl(NH_3)_5]Cl_2$, yet again the bond lengths do not appear to be significantly affected. We believe that such results may be quite general if structural comparisons are only made between precisely determined structures.

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Structure of a Five-Coordinate Copper(II) Monocomplex with the Rigid Tridentate Ligand *N*-(6-Methyl-2-pyridylmethylene)-2-(2-pyridyl)ethylamine: $[CuBr_2(C_{14}H_{15}N_3)]$

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Abstract. Dibromo[*N*-(6-methyl-2-pyridylmethylene)-2-(2-pyridyl)ethylamine]copper(II), $M_r = 448·3$, monoclinic, $P2_1/c$, $a = 8·636$ (3), $b = 12·165$ (1), $c = 15·021$ (4) Å, $\beta = 92·72$ (2)°, $V = 1576$ (2) Å^3, $Z = 4$, $D_m = 1·9$ (1), $D_x = 1·89$ g cm^{-3}, λ(Cu $K\alpha_1$) = 1·54059 Å, μ(Cu $K\alpha$) = 85·06 cm^{-1}, $F(000) = 868$, $T = 294$ K, final $R = 0·036$ for 1137 observed reflections. The structure consists of monomeric $[C(pymep)Br_2]$ molecules. The pymep ($C_{14}H_{15}N_3$) tridentate ligand and the bromine ions coordinate to the copper(II) ion to form a distorted trigonal bipyramid. Both reflectance and ESR spectra are in good agreement with the molecular structure.

Introduction. The study of the title compound is a continuation of the investigation of copper(II) complexes with tridentate ligands. The copper(II) ion forms two types of metallic complexes when it reacts with one tridentate ligand, L_{III}. The biscomplexes, $[Cu(L_{III})_2](Y)_2$ ($Y = PF_6^-$, NO_3^-), corresponding to a ratio of metal to L_{III} of 1:2, are always discrete molecules in which the metallic cation is hexacoordinated by two molecules of the tridentate ligand (Allman, Henke & Reinen, 1978; Arriortua, Rojo, Amigó, Germain & Declercq, 1982). The monocomplexes $[Cu(L_{III})X_2]$ (X = halide), ratio of metal to L_{III} 1:1, are five-coordinate discrete molecules, with a geometry around the copper(II) ion near to that of a regular square pyramid (Henke, Kramer & Reinen, 1983; Rojo, Vlasse & Beltrán, 1983); however, the rigidity of the tridentate ligand or packing effects in the unit cell may lead towards an unusual C_{2v} symmetry (Arriortua, Mesa, Rojo, Debaerdemaeker, Beltrán, Stratemeier & Reinen, 1988).

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In previous papers, we have indicated that the $[Cu(L_{III})X_2]$ monocomplexes can be utilized as precursors in the synthesis of the polynuclear species $[Cu(L_{III})X](Y)$ (Rojo, Mesa, Arriortua, Savariault, Galy, Villeneuve & Beltrán, 1988). Tridentate rigid 'quasi-planar' ligands such as terpy (2,2′:6′,2″-terpyridine) and paphy (2-pyridinecarbaldehyde 2-pyridylhydrazone) favour the stacking of $[Cu(L_{III})X]^+$ entities to give dimers (Rojo, Arriortua, Darriet, Villeneuve, Beltrán & Ruiz, 1987; Rojo, Arriortua, Mesa, Cortés, Villeneuve & Beltrán, 1987) or other condensed systems (simple or ladder-like chains) (Rojo, Mesa, Arriortua, Savariault, Galy, Villeneuve & Beltrán, 1988). The ultimate nature of the resulting compound is determined mainly by the rigid tridentate ligand and the character of the potentially bridging X anion.

In order to understand the influence of the rigidity of the tridentate ligand on the nature of these monocomplexes, we here present the crystal structure of the title compound, which contains the *N*-(6-methyl-2-pyridylmethylene)-2-(2-pyridyl)ethylamine tridentate ligand that has less rigidity than the other ligands (terpy, paphy) mentioned above.

Experimental. $[Cu(pymep)Br_2]$ was synthesized by the 1:1 reaction of *N*-(6-methl-2-pyridylmethylene)-2-(2-pyridyl)ethylamine with $CuBr_2$ in ethanol. Prismatic crystals were obtained by slow evaporation of an aqueous solution containing the compound. The density was measured by flotation in a chloroform/1,1,2,2-tetrabromoethane mixture. Analysis: calculated for $[CuBr_2(C_{14}H_{15}N_3)]$, C 37·5, H 3·3, N 9·4, Cu 14·2%; found, C 37·6, H 3·3, N 9·5, Cu 14·0%.

A specimen of dimensions 0·04 × 0·05 × 0·35 mm was selected. Preliminary cell dimensions and space-group symmetry were obtained from Weissenberg and oscillation photographs. The crystal was mounted on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Cu *Kα* radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $16 \leq 2\theta \leq 30°$.

Table 1. *Final fractional coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* (Å²) *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	7095 (1)	2619 (1)	5830 (1)	4·282 (13)
Br(1)	8096 (1)	1049 (1)	6750 (1)	4·306 (12)
Br(2)	6068 (1)	4302 (1)	6566 (1)	4·298 (5)
N(1)	4984 (10)	1912 (6)	5719 (6)	3·516 (20)
N(2)	7198 (13)	2735 (9)	4513 (6)	6·088 (42)
N(3)	9263 (9)	3297 (6)	5741 (6)	3·064 (12)
C(1)	4256 (16)	1712 (10)	6464 (9)	4·937 (14)
C(2)	2819 (17)	1262 (10)	6506 (11)	5·664 (12)
C(3)	2076 (16)	979 (10)	5719 (13)	5·938 (41)
C(4)	2748 (21)	1144 (12)	4952 (11)	6·080 (17)
C(5)	4184 (19)	1596 (11)	4978 (9)	5·759 (20)
C(6)	5230 (38)	1612 (22)	4094 (12)	9·593 (70)
C(7)	5825 (31)	2572 (29)	3896 (12)	12·494 (96)
C(8)	8498 (17)	3112 (11)	4232 (8)	4·576 (25)
C(9)	9690 (13)	3422 (8)	4896 (7)	3·727 (10)
C(10)	11080 (17)	3842 (9)	4668 (9)	4·727 (12)
C(11)	12137 (15)	4136 (9)	5349 (12)	5·170 (23)
C(12)	11770 (16)	4022 (9)	6197 (9)	5·089 (17)
C(13)	10302 (14)	3597 (7)	6391 (7)	3·475 (9)
C(14)	9898 (19)	3474 (12)	7341 (8)	5·769 (27)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu—Br(1)	2·488 (2)	Cu—Br(2)	2·509 (2)
Cu—N(1)	2·016 (8)	Cu—N(2)	1·989 (9)
Cu—N(3)	2·056 (8)	Cu—Cu^{i}	7·212 (2)
N(1)—C(1)	1·33 (2)	C(1)—C(2)	1·36 (2)
C(2)—C(3)	1·36 (2)	C(3)—C(4)	1·33 (2)
C(4)—C(5)	1·36 (2)	N(1)—C(5)	1·34 (2)
C(5)—C(6)	1·64 (3)	C(6)—C(7)	1·32 (4)
C(7)—N(2)	1·48 (2)	N(2)—C(8)	1·30 (2)
C(8)—C(9)	1·45 (2)	N(3)—C(9)	1·35 (1)
C(9)—C(10)	1·36 (2)	C(10)—C(11)	1·38 (2)
C(11)—C(12)	1·33 (2)	C(12)—C(13)	1·41 (2)
N(3)—C(13)	1·34 (1)	C(13)—C(14)	1·49 (2)
N(1)—Cu—N(2)	91·8 (4)	N(1)—Cu—Br(1)	90·4 (2)
N(1)—Cu—Br(2)	92·7 (2)	N(3)—Cu—N(2)	79·8 (4)
N(3)—Cu—Br(1)	92·9 (2)	N(3)—Cu—Br(2)	92·5 (2)
N(1)—Cu—N(3)	171·4 (4)	N(2)—Cu—Br(1)	125·2 (3)
N(2)—Cu—Br(2)	114·4 (3)	Br(1)—Cu—Br(2)	120·16 (8)
N(1)—C(1)—C(2)	125 (1)	C(1)—C(2)—C(3)	117 (1)
C(2)—C(3)—C(4)	120 (1)	C(3)—C(4)—C(5)	118 (1)
C(4)—C(5)—N(1)	125 (1)	C(5)—N(1)—C(1)	114 (1)
Cu—N(1)—C(1)	118·0 (8)	Cu—N(1)—C(5)	128·4 (9)
N(1)—C(5)—C(6)	113 (1)	C(5)—C(6)—C(7)	115 (2)
C(6)—C(7)—N(2)	107 (2)	C(7)—N(2)—C(8)	121 (1)
N(2)—C(8)—C(9)	118 (1)	C(8)—C(9)—N(3)	114 (1)
Cu—N(3)—C(13)	129·8 (7)	Cu—N(3)—C(9)	113·4 (7)
Cu—N(2)—C(7)	123 (1)	Cu—N(2)—C(8)	115·3 (8)
C(4)—C(5)—C(6)	121 (1)	C(10)—C(9)—C(8)	122 (1)
C(13)—N(3)—C(9)	116·8 (9)	N(3)—C(9)—C(10)	124 (1)
C(9)—C(10)—C(11)	118 (1)	C(10)—C(11)—C(12)	120 (1)
C(11)—C(12)—C(13)	119 (1)	C(12)—C(13)—N(3)	122 (1)
N(3)—C(13)—C(14)	119 (1)	C(12)—C(13)—C(14)	119 (1)

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.

6648 reflections were recorded in the range $2 \leq 2\theta \leq 80°$ with h $-10 \rightarrow 10$, k $0 \rightarrow 14$, l $-17 \rightarrow 17$, ω–2θ scan technique. Three orientational and two intensity control reflections were checked every 50 reflections and every hour, respectively, and showed no significant variation. Data were corrected for Lorentz–polarization and absorption effects [μ(Cu $K\alpha$) = 85·06 cm^{-1}]. The absorption correction was calculated by the Gaussian integration method, transmission values varied between 0·689 and 0·434. After averaging of the symmetry-related reflections (R_{int} = 0·014), 2681 unique reflections (of which 1137 had $I \geq 2{\cdot}5\sigma I$) were used to solve the structure. Structure solution by direct methods, using the *MULTAN*11/84 (Main, Germain & Woolfson, 1984) system, and refined by full-matrix least squares, using the *SHELX*76 program (Sheldrick, 1976). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0{\cdot}000156(F_o)^2]^{-1}$. Positions of the H atoms were computed and refined with an overall isotropic thermal parameter and anisotropic parameters for the remaining atoms. The final R was 0·036 (wR = 0·042) for all observed reflections. At the end of the refinement the maximum peak in the final ΔF map was 0·041 e Å^{-3} and $(\Delta/\sigma)_{\max} < 0{\cdot}01$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were carried out on a MicroVAX computer at the computer center of the Basque University. The geometric calculations were performed with *XANADU* (Roberts & Sheldrick, 1975) and molecular illustrations were drawn with *SCHAKAL*88 (Ketler, 1988).*

A Bruker ER 200 tt spectrometer equipped with a standard low-temperature device, operating at the X-band calibrated by an NMR probe for the magnetic field and an HP 5342A frequency counter for the microwave frequency, was used to record the ESR powder spectrum of the complex at different temperatures. The reflectance electronic spectrum at 298 K was registered on a Perkin–Elmer Lambda-9 UV/VIS/NIR spectrophotometer for a powder sample.

Discussion. Fractional atomic parameters are given in Table 1 and bond distances and angles in Table 2. Fig. 1. shows the coordination geometry of the compound with the atom-numbering scheme.

The crystal structure of the complex consists of monomeric molecules. The copper(II) ion is five-coordinated to three N atoms of the tridentate ligand [Cu—N(1),N(2),N(3); 2·016 (8), 1·989 (9), 2·056 (8) Å] and the two bromine ions [Cu—Br(1),-Br(2); 2·488 (2), 2·509 (2) Å]. The coordination polyhedron around the copper(II) ion is approximately trigonal bipyramidal. Both Br atoms and the central N(2) atom from the tridentate ligand occupy equatorial positions, while the remaining N(1) and N(3) atoms of the tridentate ligand occupy axial positions. The equatorial atoms together with the central copper(II) ion are coplanar, the major deviation from the mean plane of 0·064 (1) Å being exhibited by the metal ion.

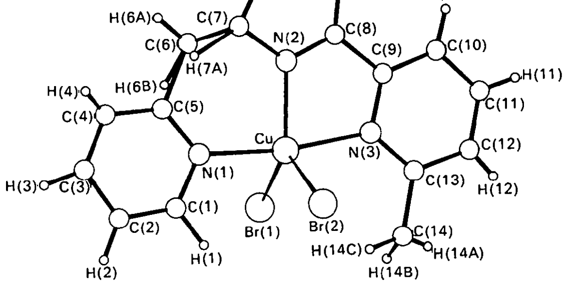

Fig. 1. Molecular structure of the complex showing the atom-numbering scheme.

Table 3. *Dihedral angles* (°) *and distortion* (Δ) *for the coordination polyhedron of the title compound, compared to ideal trigonal bipyramid* (TBP) *and regular square pyramid* (SPR) *geometries*

Dihedral angle	TBP	[Cu(pymep)Br$_2$]	SPR
δa_1	101·5	94·6	121·8
δa_3	101·5	103·7	121·8
δa_4	101·5	97·2	121·8
δa_6	101·5	100·4	121·8
δa_2	101·5	97·2	73·9
δa_5	101·5	94·6	73·9
δe_1	53·1	58·3	73·9
δe_2	53·1	69·1	73·9
δe_3	53·1	48·3	0
Δ*	0	0·22	1

* $\Delta = |[(\delta a_1 + \delta a_3 + \delta a_4 + \delta a_6) - 406{\cdot}0]/182{\cdot}7| + |[(\delta a_2 + \delta a_5) - 203{\cdot}0]/248{\cdot}4| + |[(\delta e_1 + \delta e_2) - 106{\cdot}2]/187{\cdot}2| + |(53{\cdot}1 - \delta e_3)/477{\cdot}9|$.

In the coordination polyhedron, the equatorial angles N(2)—Cu—Br(1), N(2)—Cu—Br(2) and Br(1)—Cu—Br(2) are 125·2 (3), 114·4 (3) and 120·16 (8)°, respectively. The value of the angles N(axial)—Cu—Atom(equatorial) is near to 90°, and the axial angle N(1)—Cu—N(3) is 171·4 (4)°. The departure of these angles from the ideal values of a regular trigonal bipyramid is due to the nature of the tridentate ligand. On the other hand, the distortion of the coordination polyhedron, from trigonal bipyramid (Δ = 0) towards a regular square pyramid (Δ = 1), has been calculated by quantification of the Muetterties & Guggenberger description (Muetterties & Guggenberger, 1974; Mesa, Arriortua, Lezama, Pizarro, Rojo & Beltrán, 1988). The value obtained, $\Delta = 0{\cdot}22$ (Table 3), is in good agreement with a topology near to trigonal bipyramidal.

The bond distances and angles in the tridentate ligand agree well with those reported in similar complexes (Larramendi, Díaz, Mesa, Rojo, Vía & Arriortua, 1990; Rojo, Larramendi, Durán, Mesa, Vía & Arriortua, 1990). Both pyridine rings are planar. The angle between the mean planes of these pyridine rings is 3·6 (4)°. The short N(2)—C(8) bond length [1·32 (2) Å] is in the normal range observed for NC double bonds.

The X-band ESR spectrum, from a powdered sample of the compound, is reversed axial ($g_\perp$ =

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and an X-band ESR spectrum of a powdered sample of the compound have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53661 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·177, $g_{\parallel} = 2{\cdot}065$) and remains unchanged over the temperature range 298–4·2 K. The reflectance electronic spectrum shows, in the visible region, one broad and unresolved band centred about 12000 cm^{-1}. These spectroscopic results are consistent with a geometry around the copper(II) ion near to trigonal bipyramidal (Reinen & Friebel, 1984; Hathaway & Billing, 1970), in good agreement with the crystal structure of the complex.

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Structure of Aquadibromobis(1,2,4-triazolo[1,5-*a*]pyrimidine-*N*3)copper(II), a One-Dimensional Alternating Copper(II)···Oxygen Array

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Abstract. $C_{10}H_{10}Br_2CuN_8O$, $M_r = 481{\cdot}6$, orthorhombic, $Pccn$, $a = 8{\cdot}886\,(8)$, $b = 15{\cdot}025\,(7)$, $c = 11{\cdot}928\,(5)$ Å, $V = 1592{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}98\,(5)$, $D_x = 2{\cdot}01$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·710730 Å, $\mu = 6{\cdot}313$ mm^{-1}, $F(000) = 932$, $T = 293$ K, final $R = 0{\cdot}024$ for 1111 unique observed reflections. The molecular unit contains two molecules of 1,2,4-triazolo[1,5-*a*]pyrimidine, coordinating through N3 to a copper(II) ion, two bromide ions and one water molecule completing a trigonal bipyramidal environment around copper. Both non-coordinating ligand N4 atoms of each molecule are involved in hydrogen bonding to the water ligand of the next neighboring molecule. In this way the Cu and O atoms form a one-dimensional alternating array. Cu—N 1·969 (3), Cu—Br 2·4661 (4), Cu—O 2·239 (4) Å, the N—Cu—N angle is almost linear, 177·2 (2)°. Nonbonding distances: Cu···O 3·725 (4) and N···O 2·937 (3) Å.

Introduction. Transition-metal compounds of purine analogs have been studied very often to elucidate the role of such metal ions in interaction with DNA and RNA. Most emphasis has been placed on pharmaceutically and biologically important metals, copper, platinum and zinc. Reviews have been